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Bi Addition Effect on J_C-B Performance of Powder-in-Tube Processed MgB_2 Tapes

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***Abstract*—MgB_2 tapes with 5 at.% Bi addition were fabricated through the *in situ* powder-in-tube method. Heat treatment was carried out at 700°C and 800°C for 1 h. The phase, microstructure, superconductivity and flux pinning ability were characterized by XRD, SEM, magnetic and transport measurements. The critical current density J_c and J_c-B performance for the doped and undoped samples are also given. It is found that nano-Bi doping decreased the magnetic field sensitivity of J_c, indicating an improvement of flux pinning. At 4.2 K, 10 T, J_c values of the Bi doped tapes enhanced about 2.5 times compared to that of undoped samples. The mechanism for improved J_c-B performance of Bi-doped MgB_2 tapes is investigated.**

***Index Terms*—Critical current property, doping effect, MgB_2, microstructure.**

I. Introduction

THE discovery of superconductivity in MgB_2 initiated enormous scientific interests not only in basic physics but also in practical applications. It is found that the critical temperature of MgB_2 can be over 39 K, surprisingly high for a simple binary compound. Recent progresses in MgB_2 research have made us aware of materials that may be competitive with well established A15 conductors used in MRI and NMR magnet applications. In particular, progress in cryocooler development and accessibility of cryogen free cooling at the level of 20–30 K may actually promote the technological applications of this class of materials.

The fabrication of MgB_2 wires and tapes has been extensively studied using a so-called powder-in-tube (PIT) technique with two different methods. One is an *ex situ* method in which commercially available or self-prepared MgB_2 powders are packed into a tube. The other is an *in situ* method in which constitute powders such as Mg and B are packed into a metallic tube and then, MgB_2 phase is formed inside the tube by heat treatment. Both of the methods are successful at producing MgB_2 wires and tapes with a respectable current carrying performance [2].

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However, critical current density (J_c) of MgB_2 drops rapidly in magnetic fields due to the poor flux pinning ability. The origin of flux jump is related to the thermo-magnetic instability of the motion of magnetic vortices in a type II superconductor. It is well known that the flux jump can result in a large-scale flux avalanche in the critical state, which could have a devastating consequence in such practical applications as energy storage and power transmission. For practical applications, one has to develop a method to increase the flux pinning in MgB_2.

In general, local weak or nonsuperconducting region, such as defects in the crystal lattice, dislocations, twin boundaries, grain boundaries, small precipitates, compositional fluctuations and artificial defects produced by irradiation technique, can act as effective pinning sites. Different approaches, such as doping with elements or compounds [3]–[6], hot isostatic pressing [7], irradiation with heavy ions [8] and magnetic field process [9], have been tried in order to increase J_c without significantly changes the critical temperature. Among all these techniques, chemical doping/addition, especially doping with nano- particles, seems to be the best route to improve the flux pinning and the upper critical field (H_{c2}) of MgB_2 [10], [11]. By creating scattering centers for charge carriers via chemical doping, it will be pushed to the dirty limit by shortening the mean free path of the charge carriers. However, this scattering should not affect the c-axis parameter with a significant shift of a-axis parameter. Therefore, the doping materials have to satisfy certain criteria to be acceptable as pinning centers. The presence of doping materials should not affect the formation of superconducting phase and they should not agglomerate themselves. Many different elements and compounds have been added to MgB_2 to try to improve the superconducting properties. A significant number of papers have also reported a beneficial effect of metal additions [12]–[17]. Some of these metals can improve the grain linkages [11], [12], while some others can enhance the flux pining [16], [17].

In this work, Bi nano-particles were selected as doping material because of its low melting point and non magnetism character. Bi doped MgB_2/Fe tapes were fabricated using *in situ* PIT method. The Bi doping effects on the microstructure and $J_c - B$ property of MgB_2 were also investigated.

II. Experimental

Mg (325 mesh, 99.8%), B (2–5 μm, 99.99%, amorphous), and Bi (20–50 nm, 98%) powders were used as the starting materials. Mg, B powders were mixed with the nominal composition of 1:2, the Bi doping level was 5 at.%. These mixed powders were packed into Fe tubes, and then cold-rolled into tapes. The

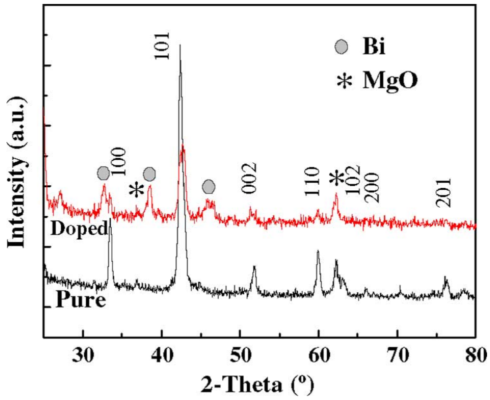

Fig. 1. XRD patterns of *in situ* processed undoped and Bi doped tapes heated at 700°C for 1 h. The peaks of MgB_2 indexed, while the peaks of MgO and Bi are marked by asterisks and circles, respectively.

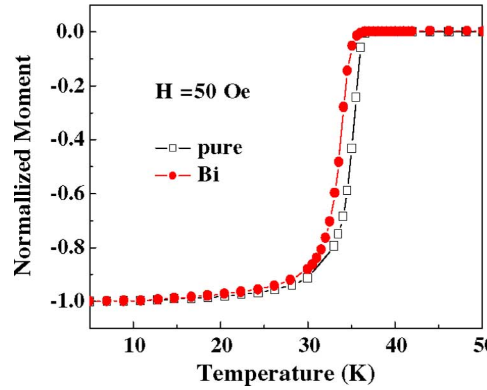

Fig. 2. Normalized magnetic susceptibility versus temperature for the doped and undoped tapes sintered at 700°C.

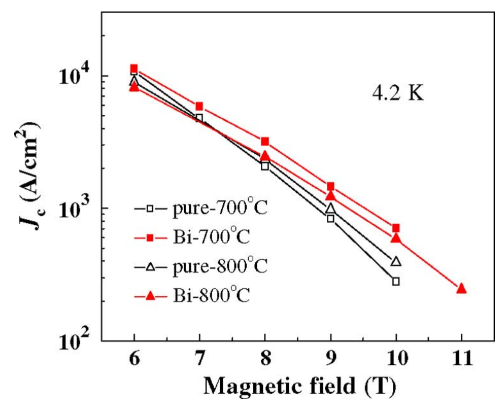

Fig. 3. J_c-B properties of undoped and Bi doped tapes heated at 700°C and at 800°C for 1 h.

detailed procedure for preparation of MgB_2/Fe tapes has been reported elsewhere [18]. The final size of the tapes was 3.2 mm in width and 0.5 mm in thickness. Undoped tapes were similarly fabricated for comparative study. These tapes were heated at 700°C and 800°C for 1 h under an Ar atmosphere, and then cooled in the furnace to room temperature.

The phase identification and crystal structure investigation were carried out using powder x-ray diffraction (XRD). Microstructure and composition analyses were performed using a scanning electron microscopy (SEM). DC magnetization measurements were performed with a superconducting quantum interference device (SQUID) magnetometer. The transport current I_C at 4.2 K and its magnetic field dependence were evaluated at the High Field Laboratory for Superconducting Materials (HFLSM) at Sendai, by a standard four-probe technique, with a criterion of 1 $\mu V \cdot cm^{-1}$.

III. Results and Discussion

A. XRD Patterns

Fig. 1 shows the XRD patterns for the 5 % Bi doped and undoped MgB_2 samples sintered at 700°C. It can be seen that undoped samples exhibit a well-developed MgB_2 phase, with only a small amount of MgO present. In the Bi doped samples, Bi appeared as an impurity phase along with MgO, but no other impurity phases can be detected. Obviously, the MgB_2 diffraction peaks were weakened in the Bi doped MgB_2 tapes, which means that phase formation of the MgB_2 was decreased.

B. Transition Temperatures

The comparison of magnetization-temperature curves between undoped and Bi doped MgB_2 tapes is shown in Fig. 2. The T_c (onset) for the undoped samples (36.5 K) was almost the same as that reported by a number of groups. For the 5% Bi doped samples, the T_c was depressed to ~35 K, but the transition widths of doped and undoped samples were almost the same. This means that metal Bi doping has little effect on the T_c property of MgB_2 tapes, which is favorable for its practical application.

C. Critical Current Properties

Fig. 3 presents the J_c in magnetic fields at 4.2 K for undoped and Bi doped samples sintered at 700°C and 800°C. Only data above 6 T are shown, because at lower field region, transport current could not be measured due to poor thermal stability. It is noted that the Bi doping enhanced the J_c values of MgB_2 tapes in magnetic fields. For the samples sintered at 700°C, J_c values of the Bi doped tapes improved about 2.5 times compared to that of undoped samples at 4.2 K, 10 T. Moreover, the sensitivity of J_c to magnetic field was decreased by Bi doping. The possible explanation for the enhancement of $J_c - B$ performance may be due to the small impurities occurred in doped samples, which improved the flux pinning ability, as will be discussed below. However, the J_c values decreased when the samples were heated at higher temperature, which is very different from nano-C doping [5].

D. Flux Pining Ability

The sensitivity of J_c to magnetic fields was decreased by the Bi doping, demonstrating an improved flux pinning ability, which could be observed clearly from Fig. 4. Here $F_p(B)$ is obtained from the hysteresis in magnetization curves and is normalized by the maximum volume pinning force F_p^{max} at the same temperature. Although the position of the maximum pinning force shifts only slightly to higher field for Bi-doped samples compared with undoped tapes, the pinning force is clearly

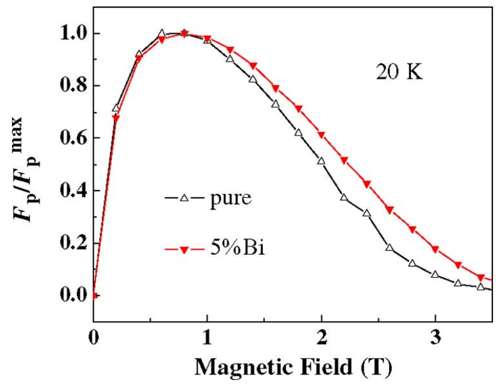

Fig. 4. Normalized volume pinning force (F_P/F_P^{max}) versus magnetic field (T) at 20 K for undoped and Bi doped tapes heated at 700°C.

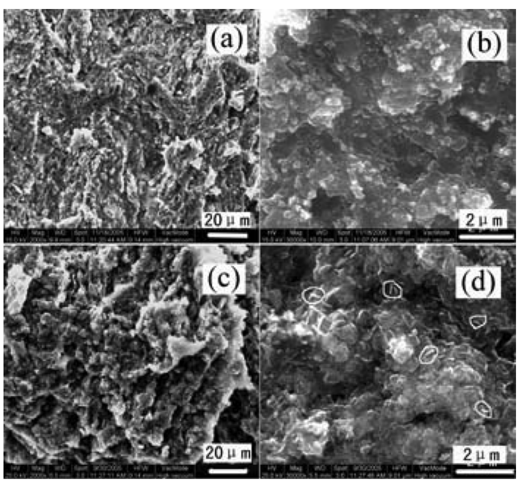

Fig. 5. SEM images of the undoped (a, b) and Bi (c, d) doped samples sintered at 700°C after peeling off the Fe sheath.

larger in the doped tapes, suggesting that pinning centers effective in a high-field region were introduced by Bi doping. And this is in accordance with the improved J_c values in high magnetic fields in Bi doped samples. It is proposed that some of the nanoscale impurities introduced by Bi doping serve as pinning centers to improve flux pinning.

E. SEM Images

Fig. 5 shows the typical SEM images of the fractured core layers for undoped and Bi doped tapes. A rough and loose microstructure is observed in the pure MgB_2 tapes (see Fig. 5(a) and (b)), while it is dense in the doped samples (see Fig. 5(c) and (d)). There is no obvious grain sizes difference between the doped and undoped samples. However, it can be seen that there are larger Bi particles existed at the MgB_2 core (see Fig. 5(d)). These particles are about 500 nm, larger than the doping Bi particles. Certainly, these larger particles will reduce the superconducting volume of MgB_2 core and decrease the superconducting current channels.

Obviously, the J_c-B performance in Bi doped MgB_2 tapes was improved. Some of the nanoscale impurities introduced by Bi doping served as pining centers. But some larger Bi particles were formed in MgB_2 core because of the low milting point of Bi element. These larger particles will lead to weak links and reduce the superconducting volume of MgB_2 core. In the case of Zr, La, or Ti doping [12], [16], [19], the elements can react with B to form intermetallics (such as ZrB_2, LaB_6, TiB_2). These reaction induced impurities contribute significantly to flux pinning and also prevent coarsening of the MgB_2, producing small grain size. However, there was no obvious reaction between Bi and MgB_2, the improvement in grain linkages was not apparent either. Consequently, the J_c values improved only slightly in Bi doped MgB_2 tapes. This result is in accordance with the conclusion that reactive metal elements additions are more beneficial in the J_c value improvement. On the other hand, if the reactions between MgB_2 and doping metal elements are very strong, such as Fe [13], Cu [16], etc., there will be a harmful effect induced by the larger amount of impurities.

IV. CONCLUSIONS

We fabricated Bi doped MgB_2/Fe tapes and investigated the Bi doping effect on the microstructure and J_c-B property of MgB_2 tapes. It is found that the J_c values and J_c-B property of MgB_2 tapes were improved by nano-Bi doping. Some of the nanoscale precipitates introduced by Bi doping were responsible for the enhancement of flux pining.

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